



# Preparation of the visible light responsive N<sup>3-</sup>-doped WO<sub>3</sub> photocatalyst by a thermal decomposition of ammonium paratungstate

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## ABSTRACT

The nitrogen doped WO<sub>3</sub> (N-WO<sub>3</sub>) photocatalyst was successfully prepared by a thermal decomposition of an ammonium paratungstate [(NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·5H<sub>2</sub>O] containing NH<sub>4</sub><sup>+</sup> ions as a nitrogen source. The N-WO<sub>3</sub> prepared at 673–873 K efficiently absorbed visible light in longer wavelength regions as compared to a commercial N-free WO<sub>3</sub>. Although small amount of Pt particles must be deposited on the catalyst surfaces, the N-WO<sub>3</sub> photocatalysts were found to decompose gaseous methanol into CO<sub>2</sub> and H<sub>2</sub>O under visible or solar light irradiations. As well as, the Pt particles on the N-WO<sub>3</sub> surfaces to enhance the photocatalytic activity showed an oxidation catalysis property at low temperatures of 323–333 K. These results suggest that the N-WO<sub>3</sub> deposited with Pt particles can effectively utilize the sunlight as light and/or heat sources.

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## 1. Introduction

TiO<sub>2</sub> semiconductor has been widely studied as a photocatalysts to purify air, water and soil polluted with various hazardous chemicals [1–3]. However, TiO<sub>2</sub> photocatalysts necessitate UV light irradiation having wavelengths shorter than 390 nm. In our previous reports, the visible light responsive TiO<sub>2</sub> photocatalysts could be successfully prepared by using ion engineering techniques such as ion implantation or RF-magnetron sputtering deposition methods [4–9]. As well as, the N-doping within the TiO<sub>2</sub> semiconductor has recently been known to be effective for the preparation of the visible light responsive photocatalysts [10–15]. In contrast, a WO<sub>3</sub> semiconductor, which shows a yellow-green color, has been expected as a photocatalyst operating under visible light irradiation. However, since the photo-excited electrons in the conduction band of WO<sub>3</sub> semiconductor cannot reduce O<sub>2</sub>, it has been believed that photocatalytic oxidation of organic compounds hardly occurs on such bare WO<sub>3</sub> surfaces. However, the WO<sub>3</sub> loaded with Pt or CuO cocatalysts have recently been reported to show the photocatalytic reactivity under visible light irradiation [16–18].

In this study, the N-doping within the WO<sub>3</sub> semiconductor was carried out in order to expand its absorption in visible light regions. As for the N-doped TiO<sub>2</sub> semiconductors, the visible light absorption generally appears only as a shoulder band at around 400–420 nm [10–12]. Moreover, the doping of large amounts of N<sup>3-</sup> anions within the TiO<sub>2</sub> lattice dramatically depresses the

photocatalytic reactivity due to the formation of Ti<sup>3+</sup> sites and/or oxygen vacancies as a recombination center for the photo-formed charge carriers. In contrast, the N<sup>3-</sup> doping into the WO<sub>3</sub> lattice is expected to hardly form the recombination centers due to an efficient charge compensation effect between W<sup>6+</sup> and N<sup>3-</sup>. The photocatalytic activity of the N-doped WO<sub>3</sub> was evaluated by the oxidation of methanol under visible or solar light irradiations as a model reaction.

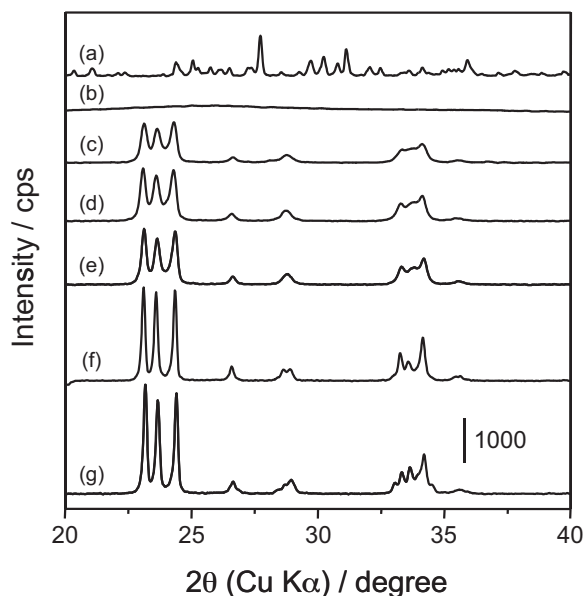
## 2. Experimental

The N-doped WO<sub>3</sub> powders were prepared by thermal decomposition of ammonium paratungstate [(NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·5H<sub>2</sub>O], Kishida Chemical Co., Ltd.) in air condition at 473–1073 K. Small amount of Pt particle was then loaded on the N-doped WO<sub>3</sub> surface by a photodeposition method from H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in aqueous methanol solution (methanol/H<sub>2</sub>O = 50 vol%). The prepared samples were denoted as Pt(X)/N-WO<sub>3</sub>(Y) (X: loading amount of Pt (wt%), Y: calcination temperature (K)). A commercial N-free WO<sub>3</sub> powder (Kishida Chemical Co., Ltd.) was used as a reference. The prepared N-WO<sub>3</sub> samples were then characterized by XRD (Shimadzu, XRD-6100), diffuse reflectance UV–vis absorption (Shimadzu, UV-2200A) and XPS (Shimadzu, ESCA-3200) measurements at room temperature.

The photocatalytic reactivity of the Pt/N-WO<sub>3</sub> samples was evaluated by decomposition of gaseous methanol under visible light or sunlight irradiations. The Pt/N-WO<sub>3</sub> catalysts (50 mg) were placed onto a quartz cell (volume, ca. 33 cm<sup>3</sup>). Prior to the photoreactions, the catalysts were degassed under high vacuum at 723 K for 2 h, treated in sufficient amounts of O<sub>2</sub> at the same temperature for

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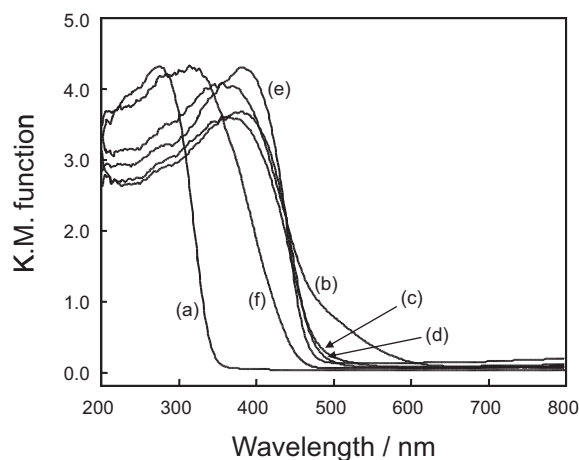


**Fig. 1.** XRD patterns of the N-WO<sub>3</sub> powders prepared by a thermal decomposition of ammonium paratungstate. (a) [(NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·5H<sub>2</sub>O], (b) N-WO<sub>3</sub>(473), (c) N-WO<sub>3</sub>(673), (d) N-WO<sub>3</sub>(773), (e) N-WO<sub>3</sub>(873), (f) N-WO<sub>3</sub>(1073), and (g) commercial N-free WO<sub>3</sub> (reference).

2 h, and then degassed at 373 K for 2 h. A gas mixture of CH<sub>3</sub>OH (0.27 kPa) and O<sub>2</sub> (0.80 kPa) was then introduced into the reaction cell. The amount of methanol introduced into the reaction cell was calculated as ca. 7 μmol. Visible light irradiation was carried out by using a 100 W high-pressure Hg lamp (Toshiba, SHL-100UVQ-2) through a cutoff filter (Toshiba Glass, L-42 (λ > 420 nm), Y-45 (λ > 450 nm) and Y-48 (λ > 480 nm)). As for the sunlight irradiation, a commercial sunlight gathering system (Laforet Engineering, XD-50D) was used [19,20]. The sunlight collected by 12 lenses is guided by a flexible optical fiber and irradiated onto the photocatalyst in the reaction cell. As well as, this system can automatically chase the highest light intensity during sunlight irradiation. To avoid the heating effect during the sunlight irradiation, the photocatalyst in the cell was cooled in a water bath. However, the water temperature increased up to 323–333 K during the photoreaction under sunlight irradiation. The amounts of CO<sub>2</sub> produced in the photocatalytic reaction were then analyzed by a gas chromatography (Shimadzu, GC-14A).

### 3. Results and discussion

Fig. 1 shows the XRD patterns of the N-doped WO<sub>3</sub>, commercial N-free WO<sub>3</sub> and ammonium paratungstate. The N-WO<sub>3</sub>(473) did not show any peaks, showing an amorphous phase. As the calcination temperatures increased up to 673 K, three sharp peaks were observed at 23–25°, which can be assigned to the (002), (020) and (200) phases of monoclinic WO<sub>3</sub> crystal [21–23]. The N-WO<sub>3</sub>(1073) showed almost same crystallinity to the commercial N-free WO<sub>3</sub>. However, the N-WO<sub>3</sub> samples did not show any



**Fig. 2.** Diffuse reflectance UV-vis absorption spectra of the N-WO<sub>3</sub> powders prepared by a thermal decomposition of ammonium paratungstate. (a) [(NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·5H<sub>2</sub>O], (b) N-WO<sub>3</sub>(673), (c) N-WO<sub>3</sub>(773), (d) N-WO<sub>3</sub>(873), (e) N-WO<sub>3</sub>(1073), and (f) commercial N-free WO<sub>3</sub> (reference).

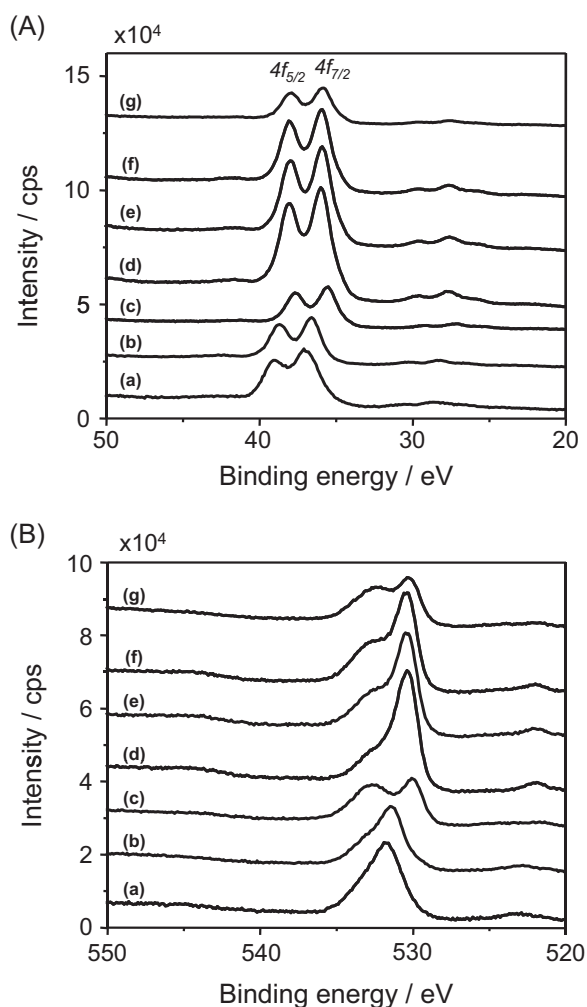
significant peak shift in the diffraction patterns, indicating that no lattice distortion was introduced by N<sup>3−</sup> doping into the WO<sub>3</sub> crystals. The primary particle sizes of the N-WO<sub>3</sub>(773), N-WO<sub>3</sub>(1073) and WO<sub>3</sub>(commercial) were determined by Scherrer's equation as 33, 67 and 59 nm, respectively. However, SEM observations revealed very large aggregated particles of 5–8 μm (data not shown here) and the BET surface areas of these samples were quite small of 3–5 m<sup>2</sup>/g.

Fig. 2 shows the diffuse reflectance UV-vis absorption spectra of the N-doped WO<sub>3</sub>, commercial N-free WO<sub>3</sub> and ammonium paratungstate. The ammonium paratungstate, which is a white powder, shows its absorption edge at around 350 nm. In contrast, as the preparation temperatures of the N-WO<sub>3</sub> increased from 673 to 1073 K, the sample colors changed from orange to yellow-green and their absorption edges were observed at around 500–600 nm. Although N-doped TiO<sub>2</sub> semiconductors are known as a visible light responsive photocatalyst, the absorption in visible light regions is generally observed as a shoulder band assigned to the formation of an impurity level due to N<sup>3−</sup> anion [10–15]. However, it is notable that the absorption edges of the N-WO<sub>3</sub> samples smoothly shift toward visible light regions as compared to the N-free WO<sub>3</sub>. This result indicates that the N<sup>3−</sup> anion doping effectively modify the bandgap structure of WO<sub>3</sub> semiconductor.

In order to discuss the surface states, the W4f and O1s XPS spectra of the N-WO<sub>3</sub> were shown in Fig. 3. The ammonium paratungstate showed peaks at 38.9 (W4f<sub>5/2</sub>) and 36.9 (W4f<sub>7/2</sub>) eV. As summarized in Table 1, these peaks can be assigned to the W<sup>6+</sup> of an insulating tungstate anion. In contrast, the N-WO<sub>3</sub> calcined at higher temperature than 673 K and N-free WO<sub>3</sub> showed typical W4f peaks at 38.0 and 35.8 eV for the stoichiometric WO<sub>3</sub> semiconductor surface [22,23]. However, since the N-WO<sub>3</sub>(473) showed the W4f peaks at a little high binding energy regions of 38.6 and 36.6 eV, the amorphous WO<sub>3</sub> surface might have a low semiconductivity. As well as, the ammonium paratungstate and

**Table 1**  
Assignments for the W4f XPS spectra of commercial N-free WO<sub>3</sub>, N-WO<sub>3</sub> and [(NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·5H<sub>2</sub>O].

Samples	Binding energy (eV)		Assignments
	W4f <sub>5/2</sub>	W4f <sub>7/2</sub>	
N-free WO <sub>3</sub> (commercial)	38.0	35.8	W <sup>6+</sup> on stoichiometric WO <sub>3</sub> surface (semiconductivity)
N-doped WO <sub>3</sub> calcined at 673–1073 K	38.0	35.8	
N-doped WO <sub>3</sub> calcined at 473 K	38.6	36.6	W <sup>6+</sup> on amorphous WO <sub>3</sub> (low semiconductivity)
Ammonium tungstate (precursor)	38.9	36.9	W <sup>6+</sup> in WO <sub>6</sub> units of polyoxo tungstate (insulation property)



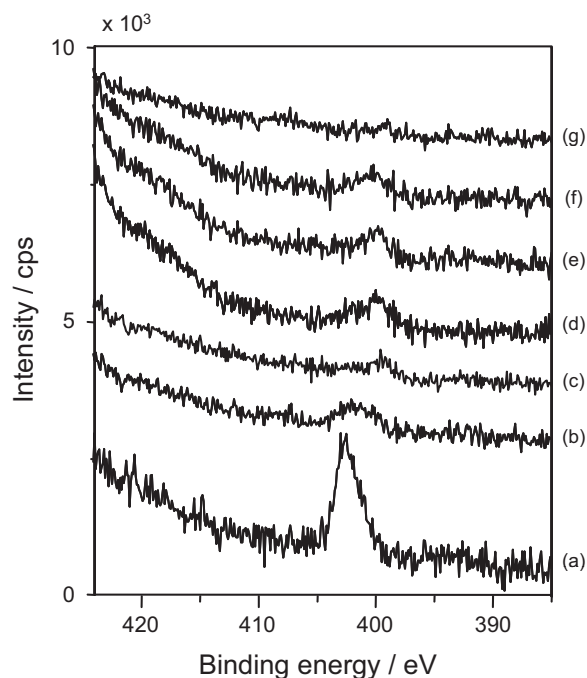
**Fig. 3.** W4f (A) and O1s (B) XPS spectra of (a)  $[(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}]$ , (b)  $\text{N-WO}_3(473)$ , (c)  $\text{N-WO}_3(673)$ , (d)  $\text{N-WO}_3(773)$ , (e)  $\text{N-WO}_3(873)$ , (f)  $\text{N-WO}_3(1073)$ , and (g) commercial N-free  $\text{WO}_3$  (reference).

$\text{N-WO}_3(473)$  showed a O1s peak at 531.4 eV, which can be assigned to the  $\text{O}^{2-}$  of an insulating tungstate anion or amorphous  $\text{WO}_3$ . In contrast, the  $\text{N-WO}_3$  calcined at higher than 673 K and commercial  $\text{WO}_3$  samples showed typical O1s spectra at 529.7 and 532.0 eV. As summarized in Table 2, the former peak can be assigned to the lattice oxygen of  $\text{WO}_3$  semiconductor [22–24]. The shoulder peak at 532 eV is often mentioned as surface hydroxyl groups. However, it should be correctly assigned to a shake-up satellite due to a transition from O2p anti-bonding orbital to W4f bonding orbital [25]. The shake-up satellite is generally observed for the semiconductor oxides, such as  $\text{NiO}$ ,  $\text{TiO}_2$ ,  $\text{Sc}_2\text{O}_3$  and etc., which have vacancies in the d- or f-orbitals. Since the shake-up satellite was not observed for the  $\text{N-WO}_3(473)$  and ammonium paratungstate, these samples do not show a semiconducting character.

**Table 2**

Assignments for the O1s XPS spectra of commercial N-free  $\text{WO}_3$ ,  $\text{N-WO}_3$  and  $[(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}]$ .

Samples	O1s (eV)	Assignments
N-free $\text{WO}_3$ (commercial)	529.7	Lattice oxygen
N-doped $\text{WO}_3$ calcined at 673–1073 K	531.9 (shoulder)	*Shake-up satellite
N-doped $\text{WO}_3$ calcined at 473 K	531.4	Amorphous $\text{WO}_3$
Ammonium tungstate (precursor)		$\text{WO}_6$ units of polyoxo tungstate



**Fig. 4.** N1s XPS spectra of (a)  $[(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}]$ , (b)  $\text{N-WO}_3(473)$ , (c)  $\text{N-WO}_3(673)$ , (d)  $\text{N-WO}_3(773)$ , (e)  $\text{N-WO}_3(873)$ , (f)  $\text{N-WO}_3(1073)$ , and (g) commercial N-free  $\text{WO}_3$  (reference).

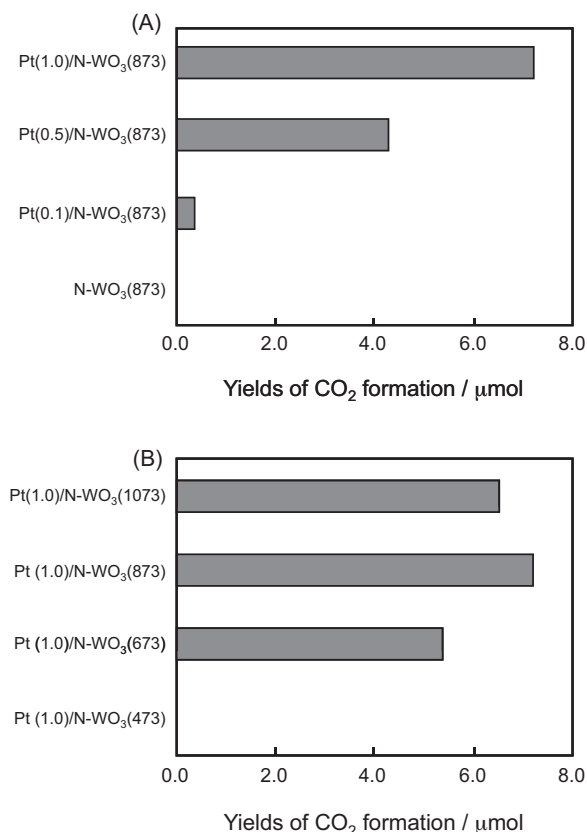
**Table 3**

Assignments for the N1s XPS spectra of commercial N-free  $\text{WO}_3$ ,  $\text{N-WO}_3$  and  $[(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}]$ .

Samples	N1s (eV)	Assignments
N-free $\text{WO}_3$ (commercial)	Not detected	
N-doped $\text{WO}_3$ calcined at 673–1073 K	ca. 400	$\text{N}^{3-}$ or $\text{NO}^{2-}$ in $\text{WO}_3$
N-doped $\text{WO}_3$ calcined at 473 K		
Ammonium tungstate (precursor)	402–403	$\text{NH}_4^+$ of polyoxo tungstate

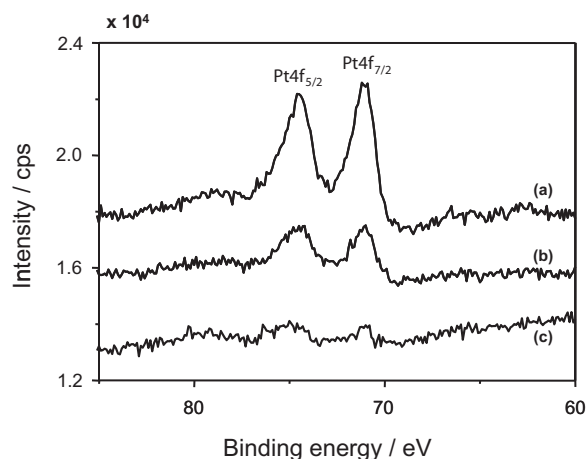
For further discussion about the surface state of the  $\text{N-WO}_3$ , the N1s XPS spectra were shown in Fig. 4 and these assignments were summarized in Table 3. The ammonium paratungstate showed a peak at 402.5 eV which can be assigned to  $\text{NH}_4^+$  ions. The  $\text{N-WO}_3$  samples showed a quite small peak at ca. 400 eV but the commercial N-free sample did not show any N1s peaks. Since the W–N bond in tungsten nitride is generally observed at 397.2 eV [26,27], the peak at 400 eV is supposed to be  $\text{N}^{3-}$  or  $\text{NO}^{2-}$  anions on the  $\text{WO}_3$  surface.

The photocatalytic reactivity of the  $\text{N-WO}_3$  was evaluated by the oxidation of methanol under visible light irradiation as a model reaction. Fig. 5(A) and (B) shows the effects of Pt loading amounts and preparation temperatures on the photocatalytic reactivity, respectively. As Abe et al. [16] have already mentioned, the  $\text{N-WO}_3(873)$  without Pt loading did not show any photocatalytic reactivity. In contrast, the  $\text{N-WO}_3(873)$  loaded with Pt was found to efficiently decompose methanol into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  under

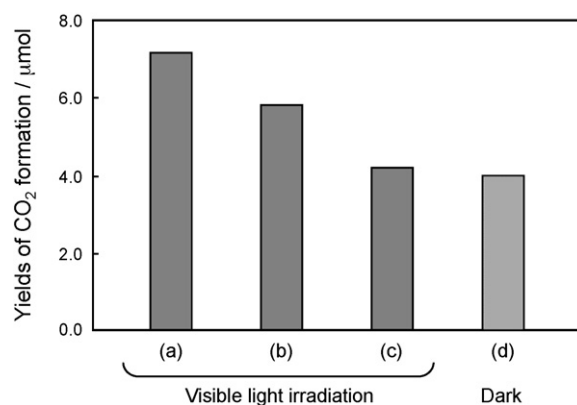


**Fig. 5.** Effects of Pt loading amounts (A) and preparation temperatures (B) on the photocatalytic reactivity for oxidation of methanol with O<sub>2</sub> on the N-WO<sub>3</sub> under visible light irradiation ( $\lambda > 420$  nm).

visible light irradiation ( $\lambda > 420$  nm). Since the initial concentration of methanol was ca. 7 μmol, the conversion to decompose methanol into CO<sub>2</sub> for the Pt(1.0)/N-WO<sub>3</sub>(873) reached to almost 100%. From this result, the optimum amount of Pt to enhance the photocatalytic reactivity of the N-WO<sub>3</sub> was adjusted to 1.0 wt%. Moreover, as shown in Fig. 5(B), the Pt(1.0)/N-WO<sub>3</sub>(873) showed the highest photocatalytic reactivity among the samples prepared at higher temperature than 673 K. However, the amorphous N-WO<sub>3</sub>(473) loaded with Pt did not show any photocatalytic reactivity.



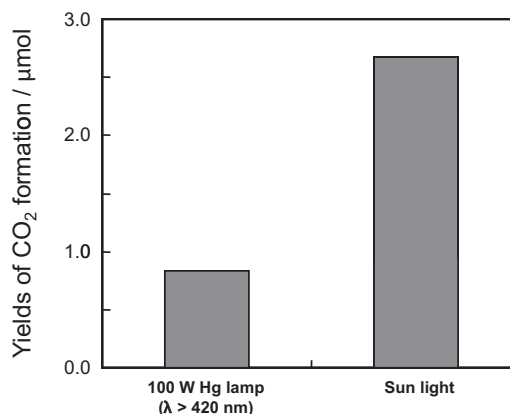
**Fig. 6.** Pt4f XPS spectra of the Pt-loaded N-WO<sub>3</sub> samples. (a) Pt(1.0)/N-WO<sub>3</sub>(873), (b) Pt(0.5)/N-WO<sub>3</sub>(873), and (c) Pt(0.1)/N-WO<sub>3</sub>(873).



**Fig. 7.** Effect of the wavelengths of incident visible light on the photocatalytic reactivity of the Pt(1.0)/N-WO<sub>3</sub>(873). (a)  $\lambda > 420$  nm, (b)  $\lambda > 450$  nm, (c)  $\lambda > 480$  nm, and (d) under dark at 323 K.

In order to discuss the chemical state of Pt cocatalyst on the N-WO<sub>3</sub>(873), the XPS measurements were carried out. As shown in Fig. 6, the Pt/N-WO<sub>3</sub>(873) samples showed the photoelectron emission at 74.5 (Pt4f<sub>5/2</sub>) and 71.1 (Pt4f<sub>7/2</sub>) eV. Since the Pt4f<sub>7/2</sub> peaks for a Pt<sup>0</sup> metal and Pt<sup>2+</sup> ion are generally observed at 70.9 and 73.6–74.0 eV, respectively [28–30], the Pt cocatalyst on the N-WO<sub>3</sub>(873) is supposed to exist as a Pt<sup>0</sup> metal, not as oxidized PtO or PtO<sub>2</sub>.

Fig. 7 shows the effect of the wavelengths on the photocatalytic reactivity of the Pt(1.0)/N-WO<sub>3</sub>(873) under visible light irradiations having different wavelengths ( $\lambda > 420$ , 450 and 480 nm). In fact, the commercial N-free WO<sub>3</sub> loaded with Pt also showed a similar photocatalytic reactivity to the Pt/N-WO<sub>3</sub>(873) under visible light ( $\lambda > 420$  nm) irradiation but did not under visible light ( $\lambda > 450$  nm) irradiation (data not shown here). In contrast, the Pt(1.0)/N-WO<sub>3</sub>(873) showed photocatalytic reactivity even under visible light irradiation having a wavelength longer than 480 nm. However, as shown in Fig. 2, the N-WO<sub>3</sub>(873) showed a very small absorption at around 480 nm. As well as, the sample temperature was confirmed to increase up to 323–333 K during visible light irradiation. So the catalytic reactivity under dark condition at 323 K was evaluated. As a result, the Pt particle as a cocatalyst on the N-WO<sub>3</sub> surface also showed a catalytic reactivity to oxidize methanol into CO<sub>2</sub> and H<sub>2</sub>O at 323 K. Although it is difficult to distinguish the precise distributions between photocatalytic and thermocatalytic reactivities, these results suggest that the Pt-loaded N-WO<sub>3</sub>



**Fig. 8.** Photocatalytic oxidation of methanol with O<sub>2</sub> on the Pt(1.0)/N-WO<sub>3</sub>(873) under visible light from a 100 W Hg lamp or focused sunlight irradiation. Sunlight irradiation: 11:00–15:00 (4 h).

can work as a visible light responsive photocatalyst as well as a low-temperature oxidation catalyst.

Finally, the comparison of the photocatalytic reactivity of the Pt(1.0)/N-WO<sub>3</sub>(873) under visible light from a 100 W Hg lamp or focused sunlight irradiations was shown in Fig. 8. The Pt(1.0)/N-WO<sub>3</sub>(873) was found to completely decompose methanol of ca. 1000 ppm into CO<sub>2</sub> and H<sub>2</sub>O under focused sunlight irradiation for 4 h (11:00–15:00). Since the light intensity of the focused sunlight was much higher as compared to the Hg lamp, the Pt(1.0)/N-WO<sub>3</sub>(873) showed an efficient photocatalytic reactivity. As well as, since the temperature of the reactor increased up to 318–323 K during the focused sunlight irradiation, the Pt particles on the N-WO<sub>3</sub>(873) surface also showed an efficient oxidation catalytic reactivity at low temperature.

#### 4. Conclusion

A novel N<sup>3-</sup>-doped WO<sub>3</sub> semiconductor could be prepared by a simple calcination of an ammonium paratungstate containing NH<sub>4</sub><sup>+</sup> ions. The N-WO<sub>3</sub> without Pt deposition did not show any photocatalytic reactivity. However, the Pt/N-WO<sub>3</sub> samples showed much higher photocatalytic reactivity to decompose methanol of ca. 1000 ppm in gas phase under visible light having a wavelength longer than 450 nm or focused solar light irradiations. As well as, the Pt cocatalyst loaded on the N-WO<sub>3</sub> surfaces was found to work as an efficient oxidation catalyst at low temperatures of 323–333 K. These results indicate that the newly prepared N-WO<sub>3</sub> photocatalyst loaded with Pt cocatalyst can effectively utilize sunlight as light and/or heat sources.

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